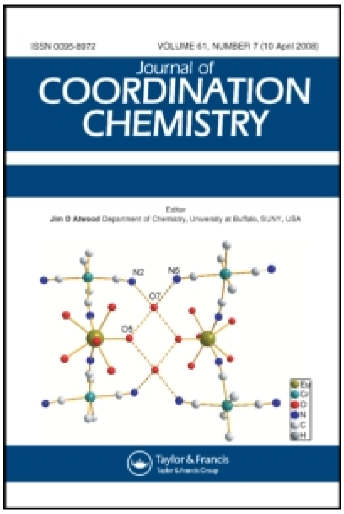

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Synthesis and spectral characterization of Schiff-base complexes derived from alanine and 2-acetylpyridine with some divalent metal acetates

Nasser Mohammed Hosny[a]
[a] Faculty of Education, Chemistry Department, Suez-Canal University, Port-Said, Egypt

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Synthesis and spectral characterization of Schiff-base complexes derived from alanine and 2-acetylpyridine with some divalent metal acetates

NASSER MOHAMMED HOSNY*

Faculty of Education, Chemistry Department, Suez-Canal University,
Port-Said 42111, Egypt

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Schiff-base complexes $[ML(H_2O)_2(Ac)]nH_2O$ ($M = Co(II)$, Ni(II) and Zn(II); L = Schiff-base ligand derived from 2-acetylpyridine and alanine and $n = 1$–$3/2$) were synthesized and characterized by elemental analysis, spectral (FTIR, UV/Vis, MS, ^{1}H-NMR), thermal (TGA), conductance and magnetic moment measurements. The results suggest octahedral geometry for all the isolated complexes. IR spectra show that the ligand coordinates to the metal ions as mononegative tridentate through pyridyl nitrogen, azomethine nitrogen and carboxylate oxygen after deprotonation of the hydroxyl group. Semi-empirical calculations PM3 and AM1 have been used to study the molecular geometry and the harmonic vibrational spectra to assist the experimental assignments of the complexes.

Keywords: Schiff base; Alanine; Metal complexes; 2-Acetylpyridine; Co(II); Ni(II) and Zn(II); Semi-empirical calculations

1. Introduction

Schiff-base complexes of amino acids play an important role in reactions of biological interest [1–3]. Some authors reported antitumor activities of Schiff bases derived from amino acids [4, 5]. Many describe metal complexes derived from salicyaldehyde and its derivatives with amino acids [6–12]. Complexes of acetylpyridines with amino acids have received much less attention, prompting us to continue our previous work [13] in synthesizing and characterizing Schiff-base complexes derived from alanine and 2-acetylpyridine with Co(II), Ni(II) and Zn(II) acetates. Reported herein are the isolated complexes with elemental analyses, spectral analyses (IR, UV-Vis, ^{1}H-NMR, MS), thermal analyses (TGA), conductance and magnetic measurements. In case of reaction products of amino acid and ketones, the band assignment was difficult. Hence, we used the semi-empirical PM3 and AM1 methods to assist the vibrational assignment of the fundamental bands.

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*Email: Nasserh56@yahoo.com

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2. Experimental

2.1. *Reagents*

All chemicals used were of analytical grade, used without further purifications.

2.2. *Technique*

Carbon and hydrogen contents were determined at the microanalytical unit of Cairo University. Metal analyses were carried out by standard methods [14]. Molar conductance measurements of the complexes (10^{-3} M) in DMSO were carried out with a conductivity bridge YSI model 32. Infrared spectra were recorded using KBr discs on a Mattson 5000 FTIR spectrometer. Calibration of the frequency was made with polystyrene film. Electronic spectra were recorded on a UV2 Unicam UV/Vis spectrometer using 1 cm stoppered silica cells. Thermal analysis measurements (TGA) were recorded on a Shimadzu model 50 instrument using 20 mg samples. The nitrogen flow rate and heating were 20 $cm^3 min^{-1}$ and 10°C min^{-1}, respectively. Mass spectra of the solid complexes were recorded on a Shimadzu GC-MS-QP 1000 Ex mass spectrometer at 70 eV at Cairo University. The ^{1}H-NMR spectrum of the Zn(II) complex in $CDCl_3$ was recorded on Bruker Avance DRx-500 instrument.

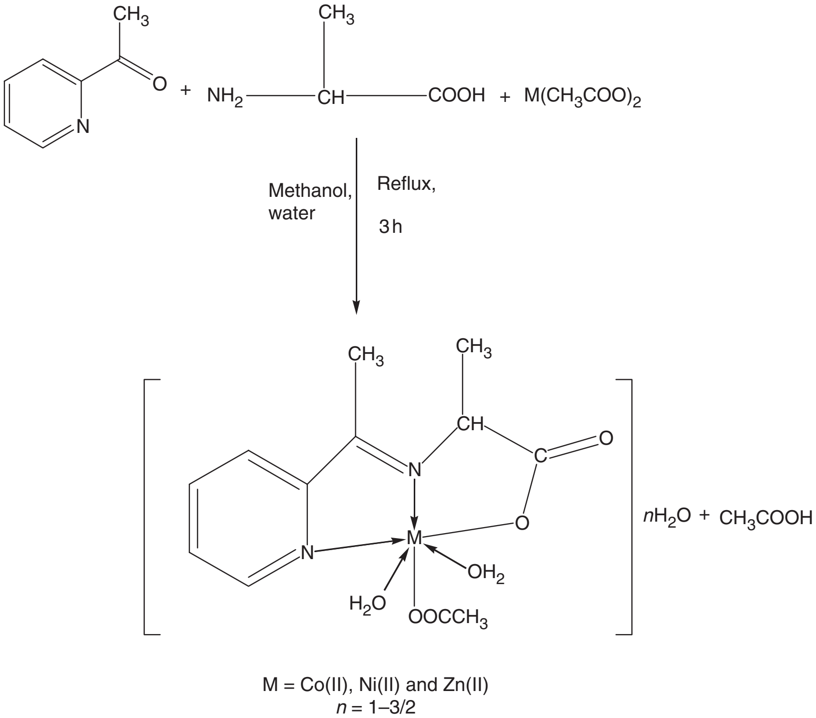
2.3. *Preparation of metal complexes by template effect*

Condensation between the NH_2 group of amino acid and the carbonyl group of aldehydes or ketones is very difficult to achieve due to the zwitterion effect, and the reaction requires special conditions. In this investigation the synthesis of metal complexes derived from the reaction of Co(II), Ni(II) and Zn(II) acetates with alanine and 2-acetylpyridine has been done using a one pot, *in situ* procedure.

Generally, an aqueous solution of alanine 0.01 mol in 10 mL water was added to 0.01 mol of 2-acetylpyridine in 10 mL methanol. The metal ions were dissolved in a minimum amount of water (5 mL), then added to the reaction mixture of the ligand dropwise with constant stirring and finally heated under reflux for 3h on a hot plate at 50°C. A fine precipitate of the solid complex has been formed. The isolated metal complexes were filtered off, washed with methanol, diethyl ether and finally with dichloromethane. The complexes were dried in a vacuum desiccator over fused calcium chloride. The formation of complexes may be represented by scheme 1.

2.4. *Computational details*

Molecular geometries of all forms of complexes were optimized using molecular mechanics and semi-empirical PM3 and AM1 methods using the Hyperchem series of programs [15]. Molecular mechanics technique was used to investigate the geometries of the suggested structures. The low lying conformers obtained from this search were then optimized at PM3 and AM1 (Polak-Ribiere) RMS 0.01 kcal. These methods are commonly used for the calculations of energy states of transition metal complexes.



Scheme 1. Scheme for formation of metal complexes.

3. Results and discussion

3.1. *Characterization of metal complexes*

The analytical data together with some physical properties of the complexes are compiled in table 1.

All the complexes are colored. The analytical data indicate that Co(II), Ni(II) and Zn(II) complexes have the general formula $[ML(H_2O)_2(Ac)]H_2O$, where L is the alanine Schiff-base ligand. The complexes are soluble in common organic solvents and partially to insoluble in water. The molar electrical conductivities of the complexes measured in DMSO were in the range $0.5–1.0\,\Omega^{-1}\text{cm}^2\,\text{mol}^{-1}$, commensurate with uncharged complexes [16]. The Schiff-base ligand forms a 1 : 1 complex, coordinating to the metal ions in a mononegative tridentate fashion.

3.2. *IR spectra*

The most important IR bands compared to the theoretically calculated values from PM3 and AM1 methods are collected in table 2. The spectra of all complexes show the disappearance of the band at $1698\,\text{cm}^{-1}$ in the free 2-acetylpyridine assignable to (C=O) (py) with the appearance of new band at $\approx 1660\,\text{cm}^{-1}$ assigned to (C=N*).

Table 1. Analytical data and physical properties of the complexes.

Compound	Color	M.P. (°C)	Formula weight	Yield (%)	Calcd (% Found)			Λ^a DMSO
					C	H	M	
$[CoL(H_2O)_2(Ac)]H_2O$	Brown	120	363.27	70	39.6(40.0)	5.8(5.3)	16.2(16.5)	0.9
$[NiL(H_2O)_2(Ac)]3/2H_2O$	Green	240	371.98	65	38.7(39.1)	5.7(5.3)	15.8(16.2)	0.8
$[ZnL(H_2O)_2(Ac)]H_2O$	Yellow	150	369.66	50	38.9(38.8)	5.4(5.3)	17.7(18.5)	0.5

[a] $\Omega^{-1}\,cm^2\,mol^{-1}$.

Table 2. Observed and calculated wave numbers (cm^{-1}) of $[CoL(H_2O)_2(Ac)]H_2O$, $[NiL(H_2O)_2(Ac)]3/2H_2O$, by PM3 and $[ZnL(H_2O)_2(Ac)]H_2O$ by AM1 semi-empirical calculations.

Co complex (Exp.)	Co complex (Calcd)	Ni complex (Exp.)	Ni complex (Calcd)	Zn complex (Exp.)	Zn complex (Calcd)	Assignment
3440(s)	3515	3450(br)	3470	3447(s)	3461	νCH ring
3145(sh)	3161	3200(sh)	3189	3340(sh)	3359	νCH ring
3100(sh)	3103	3115(sh)	3106	3180(sh)	3192	νMe
3037(sh)	3043	3070(sh)	3064	3070(sh)	3066	νMe
3000(sh)	3013	2992(w)	2980	3030(sh)	3047	νCH ring
2860(w)	2852	2850(sh)	2828	2980(w)	2960	νCH Ala
1665(sh)	1685	1670(sh)	1694	1665(sh)	1679	νCOO
1615(sh)	1649	1643(sh)	1636	1598(s)	1604	νC=N*
1568(s)	1577	1572(s)	1567	1565(w)	1547	νC=C + νC=N
1450(w)	1469	1460(w)	1459	1465(w)	1443	νCOO
1416(s)	1431	1413(s)	1412	1430(w)	1433	νCH_3COO
1343(w)	1345	1370(sh)	1358	1341(w)	1370	νC–O
1300(sh)	1281	1266(s)	1268	1310(w)	1329	νC–N
1250(sh)	1241	1215(w)	1222	1260(w)	1286	νCH_3COO
1230(w)	1212	1185(w)	1191	1210(w)	1196	δCH
1170(m)	1182	1170(m)	1174	1165(w)	1177	Ring breathing
1115(sh)	1126	1105(m)	1119	1115(w)	1120	ρCH_3
1050(m)	1049	1050(m)	1067	1068(w)	1070	γCH
890(sh)	889	920(m)	928	1021(m)	1020	νCCN
830(sh)	842	875(w)	866	965(w)	941	δCOO
669(s)	685	785(s)	770	730(sh)	720	Ring skeletal
615(m)	601	715(sh)	697	676(s)	660	γCOO
530(w)	542	510(sh)	509	630(w)	644	ρCH_3COO
515(w)	511	490(sh)	487	530(sh)	516	ρCOO
480, 425(w)	499,427	460,418(w)	453,433	505,475(w)	491,481	νM–O
405(w)	414	390(w)	416	415(w)	410	γC–C
370(w)	383	385(w)	387	367(w)	375	νM–N
280(w)	271	365(w)	363	270(w)	276	νM–Npy

ν, stretching; δ, in-plane deformation; γ, out-of-plane deformation; w, wagging; ρ, rocking; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

This behavior confirms condensation between the carbonyl of 2-acetyl pyridine and the amine group of alanine forming the Schiff base.

The Schiff-base ligand is mononegative tridentate towards Co(II), Ni(II) and Zn(II) coordinating through the pyridyl nitrogen, azomethine nitrogen and the OH group after deprotonation. This behavior is supported by the following IR evidence: the positive shifts of the bands in the regions 1595–1600, 696–676 and 460–475 cm^{-1} attributable to ν(C=C) + ν(C=N) (py), ring breathing, $Q_{i.p}$ and $Q_{o.p}$, respectively and the appearance of new bands at ~1660, 615–630 ~ 785, 530–560 cm^{-1} assigned to ν(C=N), ρ_w(COO),

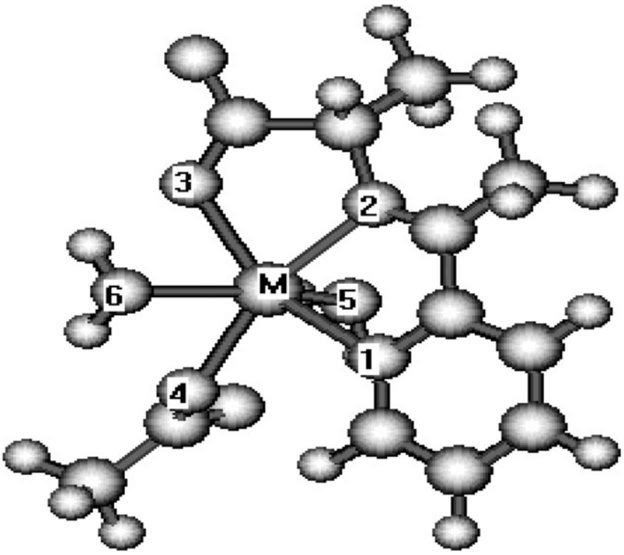


Figure 1. Suggested structure of the complexes.

δCOO and ρ_r(COO) vibrations, respectively. In addition new bands in the regions 367–385 and 418–505 cm^{-1} are assigned to ν(M–N) and ν(M–O) vibrations, respectively [17]. The presence of these bands suggests the involvement of azomethine nitrogen and carboxyl oxygen in coordination. The spectra of the complexes show two bands in the region 1413–1430 cm^{-1} and 1215–1260 cm^{-1} assigned to ν_{as} and ν_s stretching vibration of acetate group. The correlation between the positions of the antisymmetric and symmetric stretching vibrations of the acetate group and the type of coordination of this group was earlier studied [18]. It was concluded from these studies that the frequency difference between the two carboxyl stretches of ionic acetate groups is usually in the interval $\sim$167 cm^{-1}, longer values were found for monodentate and lower values for bidentate groups [17]. Correspondingly, the split of 170–198 cm^{-1} in case of Co(II), Ni(II) and Zn(II) complexes indicate monodentate acetate. This is supported by results of Ryde [19] when water is coordinated, the most stable coordination mode of acetate group is monodentate. The structures are stabilized by a very strong hydrogen bond between the noncoordinating carboxylate oxygen and the in-plane water hydrogen (figure 1).

The cause of the difference between the calculated and observed frequencies may result from the hydrogen bonded water which are not considered in the optimized molecules. Also, the experimental data were obtained from solid state, whereas the calculated harmonic frequencies are for the gas phase.

3.3. *Thermal analyses*

The thermal analyses (T.G. and D.T.G.) curves of the complexes were carried out from 25°C to 800°C. The thermal effect accompanying the changes in the solid complexes on heating are given in table 3.

Table 3. Thermoanalytical results (TG) of Co(II), Ni(II), and Zn(II) metal complexes.

Complex	T range (°C)	Mass loss Estim. (Calcd%)	Assignment
$[CoL(H_2O)_2(Ac)]H_2O$	38–117	5.6(5.0)	Loss of H_2O molecule of hydration
	119–216	9.5(9.9)	Loss of $2H_2O$ molecules of coordination
	276–308	7.1(7.7)	Loss of CO molecule
	308–425	20.0(21.4)	Loss of CH_3O and $CH(CH_3)CO_2$
	426–625	11.5(12.1)	Loss of py
$[NiL(H_2O)_2(Ac)]3/2H_2O$	43–153	7.2(7.4)	Loss of $3/2H_2O$ molecules of hydration
	153–226	9.4(9.7)	Loss of $2H_2O$ molecules of coordination
	226–263	5.6(4.0)	Loss of CH_3
	263–370	30.5(30.9)	Loss of CO_2 and $CH(CH_3)CO_2$
	370–796	20.3(21.2)	Loss of py
$[ZnL(H_2O)_2(Ac)]H_2O$	37–120	5.7(4.9)	Loss of H_2O molecule of hydration
	120–202	8.6(9.7)	Loss of $2H_2O$ molecules of coordination
	203–254	3.8(4.0)	Loss of CH_3
	246–272	9.1(11.9)	Loss of CO_2
	273–291	7.5(7.6)	Loss of CO molecule
	291–352	15.4(14.9)	Loss of CH_3 and $CH(CH_3)C$
	353–624	20.0(21.4)	Loss of py

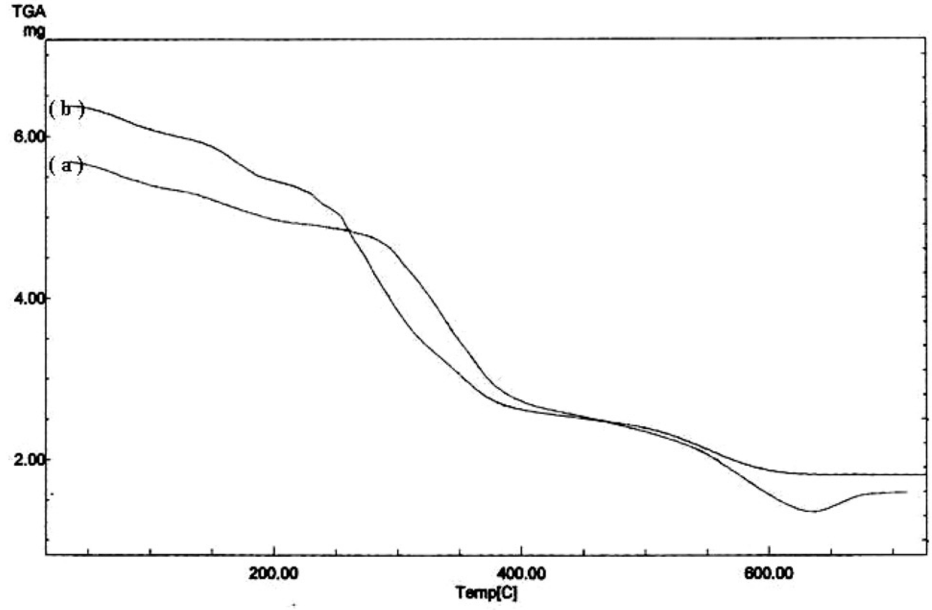


Figure 2. TG curves of (a) $[CoL(H_2O)_2(Ac)]H_2O$ and (b) $[ZnL(H_2O)_2(Ac)]H_2O$.

From the thermograms (figure 2) it is clear that $[CoL(H_2O)_2(Ac)]H_2O$ decomposes in six steps. The first step represents loss of water of hydration in the temperature range 38–117°C; Exp. (Calcd): 5.6% (5.0%). The next step is an endothermic reaction in the temperature range 119–216°C with a peak at 161°C. The mass loss observed for this process is 9.5%, close to 9.9% theoretically calculated for loss of two molecules of coordinated water. The third stage is endothermic, with maximum at 297°C. The mass loss observed for this process is 7.1%, close to 7.7% theoretically calculated for release of CO molecule from the carboxylate group of acetate. The next step in the temperature

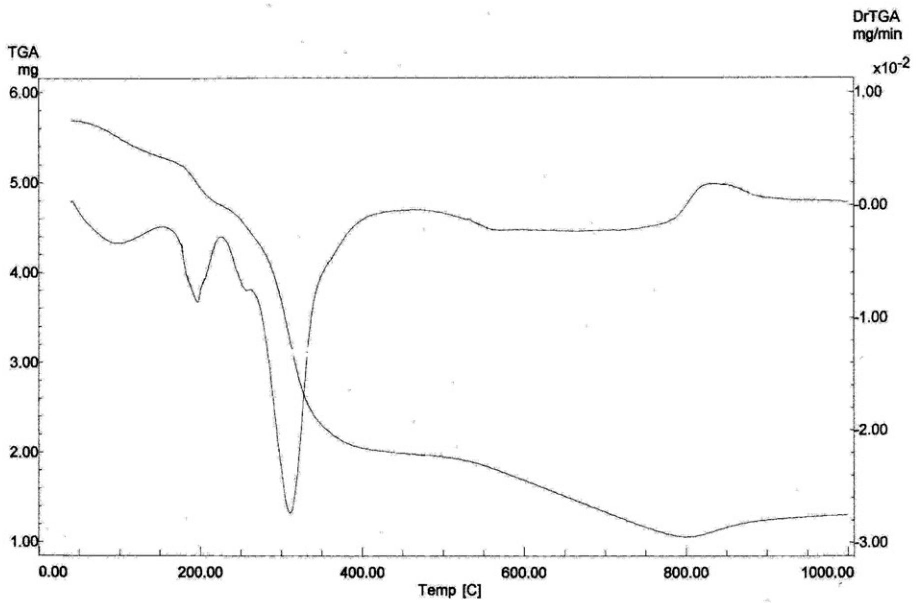


Figure 3. TG and DTG curves of [NiL(H_2O)$_2$(Ac)]3/2H_2O.

range 308–425°C corresponds to loss of the remainder of the acetate group (CH_3O) and –CH(CH_3)CO_2, 20.0%, which is close to the theoretically calculated 21.4%.

The last step is endothermic in the temperature range 426–625°C with a peak at 550°C. The mass loss observed for this step is 11.5%, close to 12.1% theoretically calculated for release of pyridyl moiety.

The thermogram (figure 3) of [NiL(H_2O)$_2$(Ac)]3/2H_2O shows release of one and half H_2O molecules of hydration in the temperature range 43–153°C. The exp. (Calcd): 7.2% (7.4%). The second step is an endothermic process in the temperature range 153–226°C, corresponding to loss of two coordinated water molecules, Exp. (Calcd): 9.4% (9.7%). The next stage corresponds to the loss of methyl group in the temperature range 226–236°C, Exp. (Calcd): 5.6% (4.0%). The fourth step represents the decomposition of the remaining acetate group CO_2 and –CH(CH_3)CO_2 in the temperature range 263–370°C, exp. (Calcd): 30.5% (30.9%). The last step in the temperature range 370–796°C corresponds to the loss of pyridyl moiety, Exp. (Calcd): 20.3% (21.2%).

The thermal analyses curves (figure 2) of [ZnL(H_2O)$_2$(Ac)]H_2O show that Zn(II) loses one water of hydration in the temperature range 37–120°C, the mass loss observed for this process amounts to 5.7%, close to the theoretically calculated 4.9%. The second step corresponds to loss of two water molecules inside the coordination sphere in the temperature range 120–202°C, Exp. (Calcd): 8.6% (9.7%). The third step in the temperature range 203–254°C corresponds to the loss of CH_3 group. The mass loss observed for this process, 3.8%, is close to the theoretically calculated 4.0%. The next step lies in the temperature range 246–272°C, corresponding to the loss of CO_2 remaining from acetate, Exp. (Calcd): 9.1% (11.9%). In the temperature range 273–291°C loss of CO from carboxyl group of 7.5% is close to the theoretically calculated 7.6%. The next step in the temperature range 291–352°C corresponds to the loss of the remaining of alanine and CH_3 of acetyl group Exp. (Calcd): 15.4% (14.9%). The next step corresponds to the loss of pyridyl moiety in the temperature range 353–624°C. The amount lost, 20.0%, is close to 21.4% theoretically calculated. In general, the stages of decomposition of the complexes can be written as shown in scheme 2.

$$[ML(H_2O)_2(Ac)]nH_2O \xrightarrow{37\text{–}153^\circ C} [ML(H_2O)_2(Ac)] + nH_2O$$

$$[ML(H_2O)_2(Ac)] \xrightarrow{119\text{–}226^\circ C} [ML(Ac)] + 2H_2O$$

$$[ML(Ac)] \xrightarrow{203\text{–}263^\circ C} [ML] + Ac$$

$$[ML] \xrightarrow{263\text{–}352^\circ C} ML^- + CH(CH_3)CO_2$$

$$ML^- \xrightarrow{352\text{–}796^\circ C} \text{Residue} + \text{py}$$

Scheme 2. General scheme of thermal decomposition of Schiff-base complexes (L = Schiff base ligand; L^- = the remainder of the Schiff base; py = pyridine and Ac = acetate).

Table 4. Electronic spectra and magnetic data of Co(II) and Ni(II) complexes.

Compound	Band position (cm^{-1})	B (cm^{-1})	β	10 Dq cm^{-1}	μ_{eff} (B.M.)
$[CoL(H_2O)_2(Ac)]H_2O$	15,748, 17,361, 22,222	744	0.77	8184	5.1
$[NiL(H_2O)_2(Ac)]3/2H_2O$	10,869, 14,705, 16,420, 18,348, 23,310	580	0.56	9850	3.3

3.4. *Electronic spectra and magnetic moments*

The electronic spectral data and the room temperature magnetic moments are listed in table 4.

The electronic spectrum of $[CoL(H_2O)_2(Ac)]H_2O$ in DMSO shows two bands at 15,748 and 17,361 cm^{-1} assigned to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) (ν_3) transitions, respectively [20]. These two bands suggest an octahedral geometry around Co(II). The spectrum also shows a band at 22,222 cm^{-1} assigned to LMCT. The ligand field parameters (table 4) [Racah parameters $B = 744$, the nephelauxetic parameters $\beta = 0.77$ and $10\,Dq = 8184\,cm^{-1}$] fall in the range for octahedral structures. The magnetic moment value 5.1 B.M. suggests the existence of an octahedral geometry around Co(II).

Electronic spectrum of $[NiL(H_2O)_2(Ac)]3/2H_2O$ in DMSO shows three bands at 10,869, 16,420 and 23,310 cm^{-1} assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(\nu_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3) transitions, respectively, indicating octahedral geometry around Ni(II) [20]. The spectrum also shows two bands at 14,705 and 18,348 cm^{-1} assigned to forbidden transitions ${}^3A_{2g} \rightarrow {}^3E_g$ and ${}^3A_{2g} \rightarrow {}^1T_{1g}$, respectively. The ligand field parameters [$B = 580$, $\beta = 0.56$ and $10\,Dq = 9850\,cm^{-1}$] fall in the range suggested for octahedral Ni(II).

3.5. *Mass spectra*

The mass spectrum of the Ni(II) complex (figure 4) shows the molecular weight corresponding to the suggested formula after loss of acetate group. The fragmentation pattern of the Ni(II) complex is represented in scheme 3.

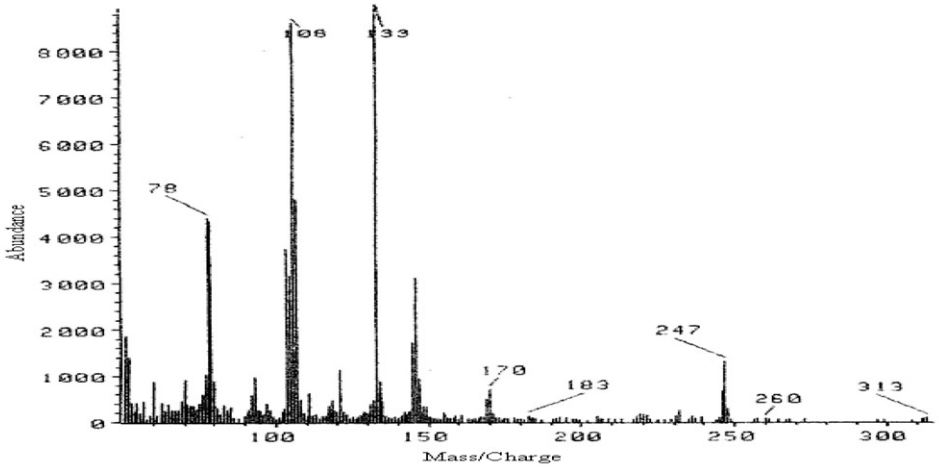


Figure 4. Mass Spectrum of $[NiL(H_2O)_2(Ac)]3/2H_2O$.

$$[\mathrm{NiL(H_2O)_2(Ac)}]3/2\mathrm{H_2O} \xrightarrow{-\mathrm{CH_3COOH}} \underset{m/z = 313\ (1.04\%)}{[\mathrm{NiL(H_2O)_2}]\ 3/2\mathrm{H_2O}} \xrightarrow{-3.5\ \mathrm{H_2O}} \underset{m/z = 248\ (3.2\%)}{[\mathrm{NiL{-}2H}]}$$

$$\underset{m/z = 171\ (2.2\%)}{\mathrm{NiC(CH_3)NCH(CH_3)COO}} \xleftarrow{-\mathrm{py}} \underset{m/z = 248\ (3.2\%)}{[\mathrm{NiL{-}2H}]} \xrightarrow{-\mathrm{NiCO_2,\ CH_3}} \underset{m/z = 133\ (100\%)}{\mathrm{pyC(CH_3)N{=}CH^{\cdot}}} \xrightarrow{-\mathrm{NCH}} \underset{m/z = 106\ (96\%)}{\mathrm{pyC(CH_3)}}$$

$$\underset{m/z = 106\ (96\%)}{\mathrm{pyC(CH_3)}} \xrightarrow{-\mathrm{CH_3C}} \underset{m/z = 78\ (49.4\%)}{\mathrm{py}}$$

Scheme 3. The fragmentation pattern of $[NiL(H_2O)_2(Ac)]3/2H_2O$.

3.6. *^{1}H NMR*

The ^{1}H NMR spectrum of the Zn(II) complex in $CDCl_3$ shows four signals at 1.8 (singlet), 2.0 (singlet), 2.6–3.6 (quartet) and 4.4 ppm (doublet) downfield with respect to TMS, assigned to protons of CH_3 (acetate), CH_3 (2-AP), CH and CH_3 (alanine) groups, respectively. The multiplet in the 7.3–8.8 ppm region is assigned to the protons of pyridine.

3.7. ***Structural parameters***

The Schiff-base ligand coordinates to Co(II), Ni(II) and Zn(II) in a mononegative tridentate manner through the pyridyl nitrogen, azomethine nitrogen and carboxylate oxygen after deprotonation from the latter group.

The distances from pyridine nitrogen to cobalt Co–N1 and nickel Ni–N1 and from azomethine nitrogen to cobalt Co–N2 and nickel Ni–N2 are shorter than the average bond distances Co–N and Ni–N in corresponding crystal structures [21, 22] by 0.20 and 0.28 Å, respectively. This behavior indicates the strong electrostatic attraction between these cations and nitrogen atoms. The distance from pyridyl nitrogen and azomethine nitrogen to zinc Zn–N1 and Zn–N2 are longer than the average Zn–N bond distance in corresponding crystal structures [23]. This behavior may be explained by the depletion of the charge on the nitrogen atom from the ring system. Distances from carboxylate oxygen to cobalt and nickel atoms are longer than the average values observed in crystal structures [21, 22] by 0.07–0.12 Å indicating depletion of charge on oxygen because of the flow of electrons from the adjacent carbonyl group.

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